

Electrochemical activation of the catalytic effect of cobalt in autoxidation of toluene in acetic acid

G. FALGAYRAC, A. SAVALL

Laboratoire de Génie Chimique, UMR 5503 CNRS, Université Paul Sabatier,
118 Route de Narbonne, 31062 Toulouse, France

Received 10 December 1997; accepted in revised form 23 March 1998

Electrochemical techniques were used to oxidize toluene in acetic acid containing cobalt(II) acetate in the absence and presence of molecular oxygen. The conditions of Co(III) generation were first studied with respect to the anodic passivation. Without oxygen, the indirect oxidation of toluene gave, by a faradaic process, mainly benzyl acetate which was then oxidized to benzoic acid, while under aerobic conditions benzoic acid was the main product, formed via the benzaldehyde by a nonfaradaic process. The initial electrochemical generation of Co(III) suppressed the induction period observed in autoxidation. Under electrolysis conditions the autoxidation process was accelerated.

Keywords: autoxidation, benzyl acetate, cobalt acetate, electrochemical activation, toluene

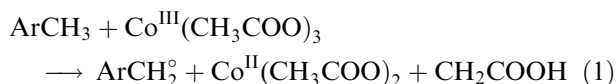
1. Introduction

The indirect electrochemical oxidation of the methyl group on substituted toluenes is carried out by regeneration at the electrode surface of a redox mediator in an aqueous solution. The mediator at a high degree of oxidation, then reacts with the substrate dissolved in the aqueous phase to give the oxidation products. To increase the overall rate of the process, the most concentrated aqueous solution mediator is used in the electrochemical reactor, and an emulsion is maintained by stirring the chemical reactor in order to have a substrate saturated aqueous phase. With the appropriate choice of mediator, the substrate oxidation can be very selective, only the methyl group is oxidized successively to alcohol, aldehyde or acid. The aromatic nucleus and the other functions are retained. The metallic mediators most often used for selective oxidation of alkylaromatics are cerium, cobalt, and manganese salts [1–4].

The Givaudan company has recently set up a procedure using a bipolar electrochemical reactor for the oxidation of substituted toluenes to the corresponding aldehydes using manganese sulphate in a sulfuric medium [5, 6]. The production of *p*-*tert*-butylbenzaldehyde is done discontinuously from *p*-*tert*-butyltoluene with an 84% selectivity and a current yield on the manganese(III) of 67%. Comninellis and Plattner [7] have oxidized different toluenes in a sulfuric medium using manganese sulfate as mediator. The current yields for the Mn(III) electroregeneration from Mn(II) are found between 35% for the oxidation of the 1,3,5-trimethylbenzene and 60% for the oxidation of the *o*-chlorotoluene. Tzédakis and Savall [8–10] obtained *p*-anisaldehyde from *p*-methoxytoluene in a sulfuric acid medium with cerium(IV) sulfate as oxidant. It was shown that the Ti–Pt anode loses

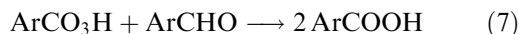
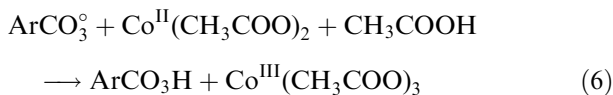
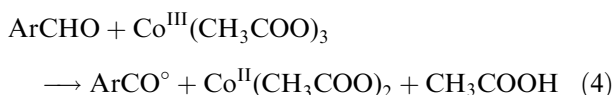
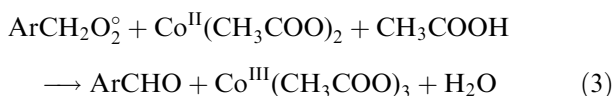
its activity at the contact with an aqueous solution saturated with *p*-methoxytoluene and it was assumed that this anode deactivation resulted from adsorption of products formed by polymerization of the aromatic substrate and its derivatives [10]. Torri *et al.* [11] carried out an indirect oxidation of *p*-methoxytoluene and *p*-*tert*-butyltoluene and obtained the corresponding aldehydes with good selectivities by using the mixed nitrate of cerium and ammonium $(\text{NH}_4)_2\text{Ce}^{\text{IV}}(\text{NO}_3)_6$ in methanol solution. Comninellis *et al.* [12] succeeded in oxidizing *o*-nitrotoluene, a compound very resistant to oxidation due to the nitro group, to *o*-nitrobenzaldehyde with yields of 80% in sulfuric acid medium (60%) at 12 °C by cobalt(III) sulfate. The *o*-nitrotoluene has also been oxidized by cerium(IV) methanesulfonate in solutions of methanesulfonic acid [13].

Under industrial conditions, the oxidation of alkylaromatics is often carried out using molecular oxygen at moderate temperatures (80–110 °C) and at low pressure (0.2 to 1 atm) in acetic acid in the presence of cobaltic acetate for concentrations of around $10^{-1} \text{ mol dm}^{-3}$ [14]. In chemical catalytic processes, toluene oxidation by molecular oxygen in the presence of cobalt salts is characterized by an induction period (generally several hours) in which Co(II) ions are oxidized to Co(III). Methyl ethyl ketone, ozone or sodium bromide can be used as an activator to reconvert Co(II) to Co(III) in the presence of oxygen [14, 15] (see farther, Reactions 8–10). The results of numerous studies on substituted toluene oxidation by molecular oxygen in the presence of cobalt acetate are compatible with the following generally accepted mechanism [16–20]:

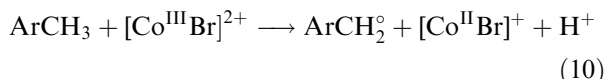
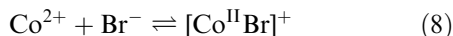


The benzylic radical reacts with the molecular oxygen to give a benzylperoxide radical which is in turn reduced by the cobalt(II) acetate, giving an aromatic aldehyde as principal product and regeneration of the cobalt(III) acetate (Mechanism 1; Reactions 2 and 3). The aromatic aldehyde can itself be oxidized in a later step to a carboxylic acid (Reactions 4 to 7) [20].

Mechanism 1: with oxygen



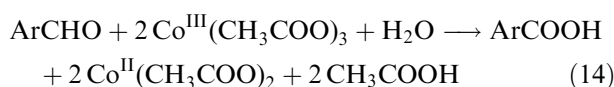
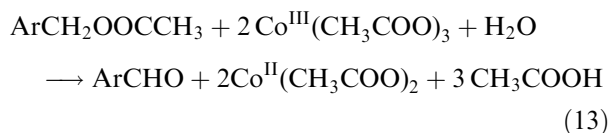
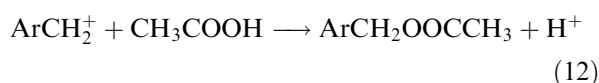
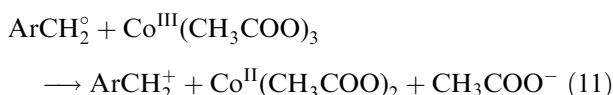
As mentioned above sodium bromide added to the medium can act as a catalyst promotor reducing the induction period (Mid Century Process [15]). The coordination of bromide ion to Co(II) may facilitate electron transfer to molecular oxygen to form Co(III)–Br complex as follows:



Unfortunately bromides are corrosive requiring a reactor with special coatings.

Under electrolysis conditions and in the absence of oxygen (Mechanism 2) benzylic acetate can be the main reaction product between the alkylaromatic and the cobalt(III) acetate (Reactions 11 and 12) [21, 22]. In the presence of a small proportion of water, benzylic acetate can in turn be oxidized successively to an aldehyde and then a carboxylic acid (Reactions 13 and 14) [21, 22].

Mechanism 2: without oxygen



Recent work carried out in the laboratory has shown that the autoxidation reactions of toluene and of *p*-methoxytoluene catalysed by cobalt(II) acetate could be favorably assisted by electrochemistry [21–24]. It has also been shown that, in the absence of oxygen, the *p*-methoxytoluene oxidation gives anisyl acetate as principal product (80% yield), whereas under bubbling oxygen *p*-anisaldehyde is obtained (40% yield) [22, 23].

In the present study we are interested in the oxidation of toluene in acetic acid medium in the presence of cobalt(III) acetate electrochemically regenerated with or without bubbling oxygen.

2. Experimental section

2.1. Electrochemical apparatus

Toluene, cobalt(II) acetate, acetic acid and sodium acetate were supplied by Aldrich and were used without additional purification. The toluene oxidation experiments and the preparation of the cobalt(III) acetate were carried out in a 150 cm³, thermoregulated Metrohm cell, which was a double glass walled cylindrical reaction vessel. Two reflux devices in series were placed at the top in order to avoid the losses of solvent and products. The voltammograms were recorded using a three electrode set up. The working electrode was a 2 mm diameter platinum disc (surface 3.14 × 10^{–2} cm²), the counter electrode was a spiral wound platinum wire. The voltammograms were recorded for a rotating platinum electrode speed of 1000 rpm. The electrodes used for the preparatory electrolyses were graphite: the anode had a surface of 21 cm² and the cathode a variable surface. All potentials were measured with respect to a saturated calomel reference electrode (SCE).

The changes in concentration of toluene and of its oxidation products during the electrooxidation reaction were monitored over time by High Pressure Liquid Chromatography (Hewlett-Packard model 1050). The reactants and the products formed were separated on an ODS C18 column (length 10 cm, internal diameter 4.6 mm) and were detected by a visible–UV spectrophotometer. The eluant was a mixture of phosphate buffer (pH 7) and methanol circulating at a flow rate of 1 cm³ min^{–1}. The phosphate buffer aqueous solution was made up of a mixture of sodium hydroxide (*C*_{NaOH} = 0.03 mol dm^{–3}) and potassium dihydrogenophosphate (*C*_{KH₂PO₄} = 0.05 mol dm^{–3}). The separation was made using a 10% to 77% methanol gradient by volume for 16 min. Qualitative identification of the products was obtained by coupling the retention time reading and the absorption spectrum recording for each product, to the wave length from the UV detector. Concentrations of the reactant and products were determined by HPLC using *p*-chlorobenzoic

acid as internal standard. Cobalt(III) acetate concentration was followed over time by UV-visible spectrophotometry at 610nm, a wavelength where only cobalt(III) absorbed.

2.2. Definitions

The yield of a reaction product is defined as the ratio of the amount of this product to the starting amount of reactant. The conversion of the starting component is the ratio of its reacted amount to its initial quantity. The molar balance is defined by the ratio of the total mole number of reactant and products assayed by HPLC on the initial mole number of reactant.

3. Results and discussion

3.1. Electrode passivation phenomena

Curve A on Fig. 1 corresponds to the residual current for a 1 mol dm^{-3} sodium acetate solution in a mixture formed with acetic acid and water at 90 and 10% by volume, respectively. Curve B corresponds to the adding of toluene (0.5 mol dm^{-3}) to the preceding solution. In this medium, toluene is only very weakly reactive at the anode. In fact, preparatory electrolyses using a constant anode current (30 mA cm^{-2}) on a graphite anode (21 cm^2) have shown that for a charge of 11 000 C toluene conversion is only 3% (solution volume: 50 cm^3 ; initial concentration of toluene 1.0 mol dm^{-3}). Benzyl acetate is mainly produced, which represents a faradaic yield of the order of 7% [21]. The addition of toluene to the acetic acid–water (90–10% by volume)–sodium acetate solution (1.0 mol dm^{-3}) also lowers the conductivity of the medium (Fig. 1, curve B). However, the corrections that can be made by estimating the ohmic drop are not sufficient to explain that, for a constant potential, the current of curve A (residual) is greater than that of curve B (residual + toluene). It is possible that toluene is adsorbed onto the platinum provoking a resistance to charge transfer which cannot be estimated using simple conductivity measurements. Curve C shows the Co(II)/Co(III) oxidation wave which gives a plateau around 2V. The presence of this plateau is clearer if the variation in the Co(II) oxidation current intensity in acetic acid–water solution is represented less the ground current as a function of the potential (Fig. 1, curve C'); the half wave potential of cobalt(II) oxidation is 1.9 V. Curve D is drawn after the addition of toluene (0.5 mol dm^{-3}) to the preceding solution and 25 min of the electrolysis at 2.3 V, on a rotating platinum electrode under nitrogen. It shows a fall in the oxidation current for cobalt(II). This passivation phenomenon similar to that observed with *p*-methoxytoluene on Ti–Pt [10], is not accentuated if the electrolysis under nitrogen is prolonged. As soon as electrolysis under oxygen at a constant potential is started, a small discrepancy between the voltammograms can be seen, indicating a

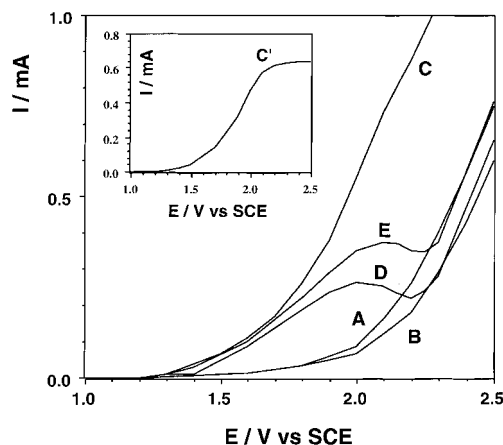


Fig. 1. Voltammograms of toluene and cobalt(II) acetate on platinum rotating electrode $\omega = 1000 \text{ rpm}$, $S = 3.14 \times 10^{-2} \text{ cm}^2$, $\Theta = 25^\circ \text{C}$. Curve A: 50 cm^3 of acetic acid–water (90–10 vol.) containing sodium acetate = (1.0 mol dm^{-3}) (residual current) under nitrogen. Curve B: solution A + toluene (0.5 mol dm^{-3}) under nitrogen. Curve C: solution A + $\text{Co}^{II}(\text{CH}_3\text{COO})_2$ (0.10 mol dm^{-3}) under nitrogen. Curve C': curve C corrected from residual current, under nitrogen. Curve D: solution A + $\text{Co}^{II}(\text{CH}_3\text{COO})_2$ (0.10 mol dm^{-3}) + toluene (0.5 mol dm^{-3}) after 25 min electrolysis at 2.3 V under nitrogen. Curve E: after curve D and 1.5 h electrolysis at 2.3 V under oxygen.

small increase in the oxidation rate. This is visible on curve E of Fig. 1 where around 2.1 V, a partial depassivation is observed.

These results show that, in acetic acid medium, it is possible to regenerate the cobalt(III) acetate from the cobalt(II) acetate and thus to oxidize the toluene in the same reactor. However, a partial passivation of the anode occurs which, in potentiostatic mode, lowers the oxidation current of the Co(II) by around 50%.

3.2. Optimization of cobalt(III) acetate preparation

As cobalt(III) acetate is not commercially available due to its instability, it must be prepared at the time of use. Two preparation methods are possible: (a) chemically by using peroxide or ozone [19, 25] and (b) electrochemically [26, 27].

Trivedi and Dhawan [27] carried out the oxidation of cobalt(II) acetate into cobalt(III) acetate on a graphite anode in acetic acid medium in a cell with and without separator. For a nondivided cell, they demonstrated that the lower the proportion of water, the higher the cobalt(III) acetate yield. Yields of 29% were obtained for a solvent composed of water–acetic acid (25%–75% by volume) and of 50% for a solution of pure acetic acid. Trivedi and Dhawan [27] studied the effect of the anodic current density on the current yield for the formation of the cobalt(III) acetate. They showed that the weaker the current density, the higher the yield: this yield was 70% for a anodic current density of 25 mA cm^{-2} . However, the effect of the cathodic current density was not studied for the reactor without separator.

The work of Trivedi and Dhawan [27] shown that graphite is a good inexpensive material, thus it was

used in place of platinum for the following preparative electrolyses of Co(III). For a fixed anodic current density (25 mA cm^{-2}), we varied the cathodic current density to examine its influence on the maximum chemical yield of cobalt(III) acetate. The graphite anode had a surface area of 21 cm^2 and the graphite cathode had an adjustable surface area so as to vary the cathodic current density while operating at a constant current of 0.5 A . The cobalt(II) acetate had an initial concentration of 0.2 mol dm^{-3} in a 1.0 mol dm^{-3} sodium acetate solution of acetic acid. The cobalt(III) acetate concentration formed by anodic oxidation tends to a steady value less than 0.2 mol dm^{-3} (100%) owing to the inverse reduction reaction at the cathode in a reactor without separator:

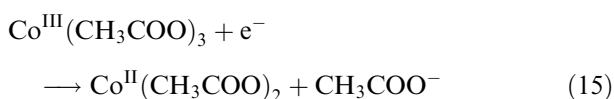


Figure 2 represents the change of the steady chemical yield of cobalt(III) acetate as a function of the applied cathodic current density. This yield goes through a maximum for a cathodic current density of 120 mA cm^{-2} . For a current density ranging between 60 and 200 mA cm^{-2} , the steady chemical yield in cobalt(III) acetate is between 45 and 50% . Beyond or below this, it decreases considerably and is around 30% for a cathodic current density of 30 or of 300 mA cm^{-2} . An interpretation is possible taking into account that operating is at constant current while the surface area of the cathode is varied.

- (i) The main reaction taking place on the cathode is hydrogen evolution; the secondary reaction being Co(III) reduction. In the range of concentration used the rate of Co(III) reduction is mass transfer limited and, on a gas evolving electrode,

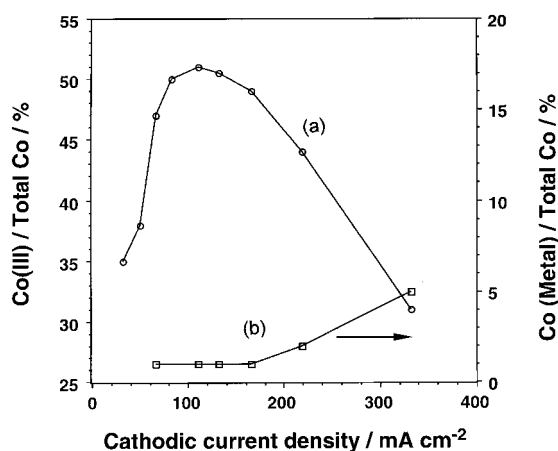


Fig. 2. $\text{Co}^{\text{II}}(\text{CH}_3\text{COO})_2$ yield and metallic cobalt yield obtained as function of cathodic current density, 100 cm^3 acetic acid containing 1.0 mol dm^{-3} sodium acetate. $\text{Co}^{\text{II}}(\text{CH}_3\text{COO})_2$: 0.20 mol dm^{-3} . Electrolysis under galvanostatic condition: $I = 0.50 \text{ A}$ (anodic current density 25 mA cm^{-2}). (a) Chemical conversion into cobalt(III) acetate; (b) metallic cobalt yield.

- the mass transfer coefficient of a reactant increases as the flux of gas evolved increases [28].
- (ii) For a weak cathodic current density, the cathodic surface area being large ($S_c = 15 \text{ cm}^2$ for $i_c = 33 \text{ mA cm}^{-2}$), the probability of contact between cobalt(III) acetate and the cathode is the highest leading to a greater reduction rate of the latter to cobalt(II) acetate. But for these conditions the hydrogen flux evolved is low and the mass transfer coefficient of Co(III) has lower values.
- (iii) When the cathode surface area decreases (that is when the cathodic current density increases), the probability of reduction of the cobalt(III) acetate to cobalt(II) acetate at the cathode decreases, which increases the steady concentration of cobalt(III) acetate to a maximum of 50% yield.
- (iv) When the cathodic current density increases again (from 150 to 330 mA cm^{-2}), the mass transfer coefficient of the cobalt(III) acetate reaches higher values at the cathode owing to hydrogen evolution [28]; this results in an increase in the Co(III) reduction rate and a decrease in the Co(III) concentration steady state value. Furthermore, when the cathodic density varies from 110 to 330 mA cm^{-2} (the respective surface areas of the cathode are 4.5 and 1.5 cm^2), the cobalt deposited in metallic form goes from 1% to 5% of the total cobalt (Fig. 2, curve (b)). Thus for current densities of 300 mA cm^{-2} , the cathode is no longer a graphite electrode but a modified electrode (graphite with deposit of cobalt metal).

3.3. Indirect electrochemical oxidation of toluene by cobalt(III) acetate under nitrogen

The indirect electrochemical oxidation of toluene (0.5 mol dm^{-3}) by cobalt(III) acetate in a deoxygenized medium gives, for a charge of 2 F mol^{-1} of toluene, benzyl acetate in 20% chemical yield and benzoic acid in 10% yield as primary products (Fig. 3). During this experiment, the initial electrolysis current was fixed at 0.9 A and was then brought to 0.45 A so as to establish a basis of comparison of the results with those for the assisted autoxidation (cf. Section 3.4). Under the same operating conditions as Fig. 3 and a constant electrolysis current of 0.9 A for 7 h (3.6 F mol^{-1}), the chemical yield in benzoic acid is thus 40% for a 60% conversion of toluene. The global faradaic yield (acetate + acid + aldehyde) after 7 h of reaction is 50% (Fig. 3); this value (less than 100%) is in agreement with Mechanism 2 (Reactions 11–14). Furthermore, a decrease in mass balance can be observed over time; this is due to the formation of secondary products detected, but not identified, by HPLC. These secondary reactions, in addition to oxygen evolution, explain the low faradaic yield observed. Some details are given by Falgayrac [21].

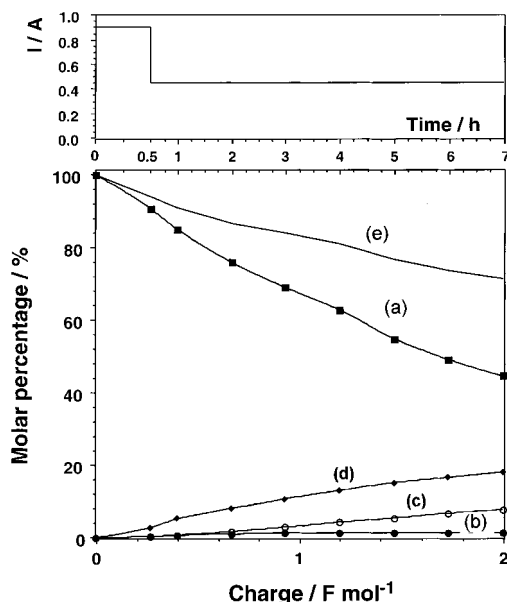


Fig. 3. Electrochemical oxidation of toluene under nitrogen bubbling. 130 cm^3 of acetic acid solution containing sodium acetate: 0.87 mol dm^{-3} . Initial concentrations: $\text{Co}^{\text{II}}(\text{CH}_3\text{COO})_2$: 0.44 mol dm^{-3} ; toluene: 0.50 mol dm^{-3} . $T = 109^\circ\text{C}$. Electrolysis under galvanostatic condition: graphite electrodes (anode 12 cm^2 , cathode 8 cm^2 , without separator). (a) Toluene; (b) benzaldehyde; (c) benzoic acid; (d) benzyl acetate (e) molar balance.

3.4. Electrochemical activation of the catalytic effect of cobalt in toluene oxidation

Under the same experimental conditions as in Fig. 3, but under bubbling oxygen, the oxidation of toluene

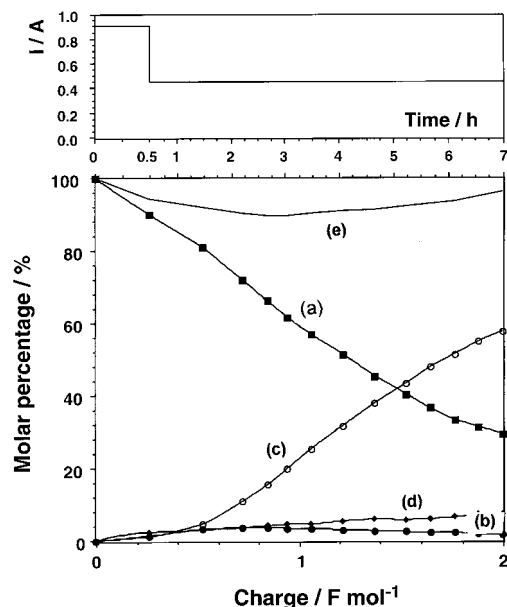


Fig. 4. Activation of the catalytic effect of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ on toluene oxidation under oxygen bubbling. 130 cm^3 of acetic acid solution containing sodium acetate: 0.87 mol dm^{-3} . Initial concentrations: $\text{Co}^{\text{II}}(\text{CH}_3\text{COO})_2$: 0.44 mol dm^{-3} ; toluene: 0.50 mol dm^{-3} . $T = 109^\circ\text{C}$. Oxygen flow rate $150 \text{ cm}^3 \text{ min}^{-1}$. Electrolysis under galvanostatic condition: graphite electrodes (anode 21 cm^2 , cathode 8 cm^2 , without separator). (a) Toluene; (b) benzaldehyde; (c) benzoic acid; (d) benzyl acetate; (e) molar balance.

leads to the same oxidation products (Fig. 4). At the beginning of autoxidation the current was fixed at a high value (0.9 A for 30 min) in order to rapidly produce enough Co^{III} concentration to start the autoxidation process, then it was reduced to 0.45 A to decrease the contribution of the indirect electrochemical oxidation with respect to that of autoxidation. Figure 4 shows that the proportion of benzoic acid formed for a charge of 2 F mol^{-1} is much higher under bubbling oxygen than under an inert atmosphere (Fig. 3). Furthermore, under bubbling oxygen the material deficit due to secondary product formation is low ($<5\%$).

If the oxidation reaction of toluene by cobalt(III) acetate were the sole reaction (Reactions 1 and 11 to 14), the benzoic acid yield for a charge of 2 F mol^{-1} would be 33% ; while here the benzoic acid yield is 60% . This result contrasts with that obtained under the same conditions but without oxygen (compare Figs 4 and 3). A short induction period (30 min) is visible at the beginning of the experiment shown on Fig. 4. The electrolysis effect is to generate Co^{III} ions which initiate the benzylic radical formation (Reaction 1) and its further reaction with molecular oxygen (Reactions 2–7). In the absence of electrolysis and of initial Co^{III} , or of a chemical initiator (e.g., NaBr), a very long induction period (several hours) is generally observed before the start of autoxidation [15, 21]. The cobalt(III) acetate is not totally consumed by its reaction with toluene as in the process of indirect electrooxidation; under aerobic conditions it is also regenerated by the autoxidation reaction (Mechanism 1, Reactions 3 and 6).

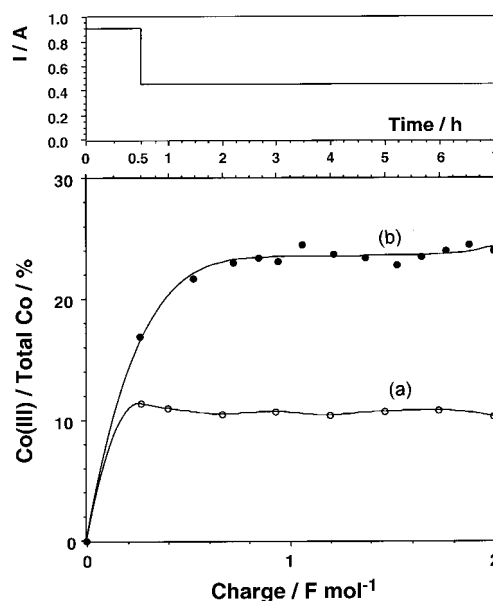


Fig. 5. Variation of $\text{Co}^{\text{III}}(\text{CH}_3\text{COO})_3$ yield during toluene oxidation. 130 cm^3 of acetic acid solution containing sodium acetate (0.87 mol dm^{-3}). Initial concentrations: $\text{Co}^{\text{II}}(\text{CH}_3\text{COO})_2$: 0.44 mol dm^{-3} ; toluene: 0.50 mol dm^{-3} . $T = 109^\circ\text{C}$. Electrolysis under galvanostatic condition: graphite electrodes (anode 21 cm^2 , cathode 8 cm^2 , without separator). (a) Under nitrogen; (b) oxygen flow rate $150 \text{ cm}^3 \text{ min}^{-1}$.

Assaying cobalt(III) acetate over time (Fig. 5) for the experiments of Figs 3 and 4 shows that its concentration increases very rapidly at the beginning of the reaction (especially during the first half hour, when the current intensity is highest) then remains steady after an hour. For the conditions used, the stationary cobalt(III) concentration is 2.5 times higher under bubbling oxygen than under bubbling nitrogen; this difference is due to the fact that, in the presence of oxygen, the cobalt(III) acetate is not only regenerated by anodic electrooxidation of the cobalt(II) acetate, but also by the oxidation of the toluene by molecular oxygen (Reactions 2–7).

4. Conclusion

This work shows that in acetic acid medium *in situ* Co(III)/Co(II) redox mediator regeneration during toluene oxidation is possible even with partial passivation of the anode.

When the indirect electrochemical oxidation of toluene by cobalt(III) acetate takes place under a nitrogen atmosphere, benzyle acetate is the primary product obtained; the latter can, in turn, be oxidized to benzoic acid. Cobalt(III) acetate is the active form consumed in the oxidation of toluene: the reaction is faradaic.

Under an oxygen atmosphere, benzoic acid is the final product. Cobalt acetate thus plays the role of catalyst, it intervenes under its two degrees of oxidation II and III in the autoxidation reaction. The main oxidant in this operating mode remains oxygen. Under electrolysis conditions the autoxidation is accelerated. The quantitative effect of electrochemical Co(III) regeneration on the autoxidation kinetics will be presented in a further paper.

Acknowledgements

We thank Electricité de France for financial support.

References

- [1] S. Torii, in 'Electroorganic Syntheses, Part I', Kodansha and VCH, Tokyo, Weinheim (1985); pp. 75–95
- [2] D. Degner, *Topics in Current Chemistry*, Springer-Verlag, **148** (1988) 1–95.
- [3] E. Steckhan, *Topics Current Chemistry*, Springer-Verlag, **142** (1987) 1–69.
- [4] P. M. Bersier, L. Carlsson and J. Bersier, *Topics in Current Chemistry*, Springer-Verlag, **170** (1994) 113–229.
- [5] P. Vaudano, *Chimia* **46** (1992) 103–6.
- [6] P. Vaudano, E. Plattner and C. Comninellis, *ibid* **49** (1995) 12–6.
- [7] C. Comninellis and E. Plattner, *J. Appl. Electrochem.* **17** (1987) 1315–8.
- [8] T. Tzedakis and A. Savall, *Eng. Chem. Res.* **31** (1992) 2475–83.
- [9] *Idem*, *Chem. Engng Sci.* **46** (1991) 2269–79
- [10] *Idem*, *J. Appl. Electrochem.* **27** (1997) 589–97.
- [11] S. Torii, H. Tanaka, T. Inokuchi S. Nakane, M. Akada, N. Saito and T. Sirakawa, *J. Org. Chem.* **47** (1982) 1647–52.
- [12] C. Comninellis, E. Plattner and P. Javet, *J. Appl. Electrochem.* **9** (1979) 753–5
- [13] J. J. Lozar and A. J. Savall, *Ind. Eng. Chem. Res.* **34** (1995) 3149–53.
- [14] R. A. Sheldon and J. K. Kochi, 'Metal-Catalysed Oxidations of Organic Compounds', Academic Press, New York (1981), p. 122.
- [15] P. Raghavendrachar and S. Ramachandran, *Ind. Eng. Chem. Res.* **31** (1992) 453–62.
- [16] E. I. Heiba, R. M. Dessau and W. J. Koehl, *J. Am. Chem. Soc.* **91** (1969) 6830–7.
- [17] E. J. Scott and A. W. Chester, *J. Phys. Chem.* **76** (1972) 1520–4.
- [18] Y. Kamiya and M. Kashima, *Bull. Chem. Soc. Jpn.* **46** (1973) 905–8.
- [19] C. F. Hendricks, H. C. A. van Beek and P. M. Heertjes, *Ind. Eng. Chem. Prod. Res. Dev.* **17** (1978) 256–60.
- [20] *Idem*, *ibid.* **17** (1978) 260–4.
- [21] G. Falgayrac, Thèse de l'Université Paul Sabatier, Toulouse (1996).
- [22] G. Falgayrac and A. Savall, *Catal. Today* **24** (1995) 189–94.
- [23] A. Savall and G. Falgayrac, in Proceedings of the 9th International Symposium on Electrosynthesis in the Chemical Industry, Sheraton Stand Key, Clearwater FA, 5–9 Nov. (1995).
- [24] D. Bejan, J. Lozar, G. Falgayrac and A. Savall, Proceedings of the 2nd International Symposium Catalysis in Multiphase Reactors, Toulouse, 16–18 March (1998).
- [25] E. Koubek and J. O. Edwards, *J. Inorg. Nucl. chem.* **25** (1963) 1401–8.
- [26] J. A. Sharp and A. G. White, *J. Chem. Soc.* (1952) 110–116.
- [27] D. C. Trivedi and S. K. Dhawan, *J. Appl. Electrochem.* **21** (1991) 504–7.
- [28] H. Vogt, in 'Comprehensive Treatise of Electrochemistry, Vol. 6, Electrode: Transport' (edited by E. Yeager, J. O'M. Bockris, B. E. Conway and S. Sarangapani), Plenum Press, New York (1983); chapter 7, pp 445–89.